

John E. Duherg

NACA TM 1338

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1338

THE OXIDATION OF METALS AND ALLOYS

By Erich Scheil

Translation

"Über das Zundern von Metalle und Legierungen." Zeit. für Metallkunde
Vol. 29, July 1937.



Washington

June 1952



X NACA TM 1338

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1338

THE OXIDATION OF METALS AND ALLOYS*

By Erich Scheil

Many metals are heat-treated with free access of air to the metallic surface, which then becomes oxidized. This is the case except for the noble metals, the oxides of which have decomposition pressures above the partial pressure of the oxygen of the air. Nitrides apparently do not form during annealing in air of the technically applied metals, or at least they do not form in appreciable amounts. More accurate investigations are yet unavailable, however. Except for the rarely formed gaseous (for example, MoO_3) or liquid (for example, V_2O_5) reaction products, there is formed during oxidation a crystallized or a glassy oxide layer on the transmissiveness and adherence of which the continuance of the oxidation process beneath the oxide layer depends.

Oxidation of Pure Metals

On the metal where oxides may occur or one of the stable oxides may be absent, oxides are formed in the order of their oxide content. The first monomolecular oxide layer is formed very rapidly. The ensuing thickening occurs by diffusion in the oxide layer. Cracks or scales in the oxide layer reduce the diffusion paths and thereby accelerate the oxidation.

If the oxide layer consists of only one type of crystal, its rate of increase in thickness dn/dz is inversely proportional to the thickness n of the oxide layer at the time z (references 1 and 2):

$$\frac{dn}{dz} = \frac{1}{Kn} \quad (a)$$

or, after integration

$$n = \frac{z}{\sqrt{2K}} = \frac{z}{K'} \quad (b)$$

*"Über das Zundern von Metalle und Legierungen." Zeit. für Metallkunde. Vol. 29, July 1937, pp. 209-214.

Where K' is a measure of the checking of the oxidation through the already existing oxide layer. Pilling and Bedworth (reference 2) found that this time law was confirmed for the majority of the metals, even when the oxide layer consisted of several oxides. According to a careful investigation by W. Feitknecht (reference 3), the oxidation of copper at first proceeds more rapidly than is indicated by the square root law. In this initial region, changes which were considered as deviations were found (reference 3) in the structure of the oxide layer. In the range of the initial coloring of the oxides, that is, for the thinnest oxide layers, G. Tammann and W. Koster (reference 4) obtained an exponential time law the interpretation of which is difficult (reference 5). Except for these initial phenomena, the square root law is well confirmed by experiment.

Several metals, however, possess quite a different time law for the oxidizing process. Figure 1 shows three oxidation isotherms of tungsten. The increase in weight was determined by weighing the specimen in the furnace. The scattering of the test points is due to the temperature fluctuations; the furnace was not regulated during the night. At 900° the oxide layer no longer adhered to the specimen, but dropped into a receiver vessel and was weighed together with the vessel (reference 6). The quantity of oxide on the 500° and 700° isotherms increased in proportion with the time. The same linear time law was obtained in reference 2 for calcium and magnesium. The test on magnesium was respected and the law was confirmed herein.

The linear time law states that the protective action of the oxide does not improve with an increase in the thickness of the layer. The result does not mean, however, that the existing oxide layer has no retarding effect on further oxidation. Because of the large velocity of the boundary-surface reaction, the metals in the case of the linear time law of oxidation must be converted so rapidly and completely into the oxide that to follow the process by weighing would be impossible. The linear time law will also be satisfied, however, if scales in the oxide layer are formed periodically. The appearance of the oxide layer, to be discussed further, is in agreement with this assumption.

The acceleration of the oxidizing process observed for the 900° isotherm can be attributed to a temperature increase of the specimen by the oxidation heat. A more marked acceleration of the oxidation above a certain temperature was found in reference 2 for calcium and magnesium.

For these two metals, the linear time law was explained by the volume reduction during the oxide formation (reference 2). According to K. Fischbeck (reference 7), in the case of the following metals, the metal has a greater volume than its oxide with the same number of atoms:

Li, Na, K, Cs, Rb, Mg, Ca, Sr.

Tungsten is missing in this series, as its volume increases about threefold during oxidation. As will be shown it is also doubtful for calcium and magnesium whether the volume decrease is the factor which explains the linear time law.

The shape of the oxidized body is different depending on the time law of the oxidation. Figure 2 shows the appearance of an oxidized copper specimen (square root law) and figure 3 shows that of an oxidized tungsten specimen (linear law). In the oxidation of the copper, an oxide layer grows on the initially sharp-edged specimen, the dimensions of which, except for the somewhat rounded edges and corners, are proportional to the dimensions of the initial specimen. On the copper, therefore, the increase in thickness of the oxide layer must be due to the formation of layers of the magnitude of the existing oxide surface; that is, the growth of the oxide layer occurs at the oxide-air boundary (reference 8).

In the case of the tungsten specimen shown in figure 3, on the contrary, the initially projecting edges receded inwards. This may be seen still more clearly in the case of a widia specimen shown in figure 4 (tungsten carbide in a cobalt matrix (reference 9)). In this specimen, the oxide layer is considerably thicker and possesses a smooth surface, particularly at the receded edges. The hollowing of the edges is explained by the growth of a layer the size of the metal-oxide surface. Generally, for a body of the form of figure 2, the thickening of the reaction layer occurs at its external surface, while for a body of the shape shown in figures 3 and 4 it occurs at its inner surface.

On the other hand, in the case of tungsten, which oxidizes with an increase in volume, the reason for the shape of figures 3 and 4 is understandable. There is no explanation for the occurrence of this shape in the case of calcium (reference 10) and magnesium. Because of the decrease in volume on oxidation, the surfaces should be concave inward instead of convex outward. The decrease in volume must therefore be offset by an increase in volume as a result of scale formation. It appears that even in the case of calcium and magnesium the reduction in the volume is not the primary factor during oxidation.

According to the investigation of reference 2, aluminum and cadmium occupy a particular position as regards the time variation of the oxidation process. After a small relatively rapid oxidizing reaction, the oxidation practically comes to a stop. Wagner (reference 11) sees the possibility of explaining this circumstance by the fact that both for aluminum (reference 12) and for cadmium (reference 13) unstable oxides are formed first.

The increased thickness of the oxide layer proceeds by diffusion. Since the bonds are heteropolar, the traveling particles are not neutral atoms but ions and electrons (reference 14). The assumption of electron travel is necessary, since otherwise at the points where an ion has departed or arrived, high electrostatic charges would rise which would prohibit the motions that actually took place. These accompanying phenomena are neglected herein, and only the travel of the ions is considered. A distinction must be made between the diffusion of the anions and the cations. The velocity of the two processes is in general so different that only the diffusion of one type of ion can be taken into account.

This is particularly the case if one of the two types of ion occurs in a number smaller than that corresponding to the ideal lattice construction. This is, for example, the case for ferrous oxide. According to Schenk (reference 15), ferrous oxide possesses a smaller iron content than is required by the stoichiometric composition FeO . Jette and Foote (reference 16) have shown, by comparing the volume obtained by the thickness determination with that obtained by x-ray methods, that the ferrous oxide lattice has unoccupied positions in the Fe^{++} ion lattice. The same is true for FeS (reference 17) and FeSe (reference 18).

In a lattice constructed in this manner, the iron ions in the neighborhood of an unoccupied position can easily interchange. The diffusion of the iron ions will therefore be larger compared with the diffusion of the oxygen ions.

In a similar manner, Dunwald and Wagner (reference 19) assume for cuprous oxide unoccupied positions in the copper ion lattice on the basis of the following observations. In electrolytic tests there was a transport of the Cu^+ ions. Furthermore, the electrical conductivity of the cuprous oxide increased with increasing oxygen pressure; that is, increasing oxygen content of the cuprous oxide resulted in an increase in the number of unoccupied places. Dunwald and Wagner computed, from their measurements for a pressure of 30 millimeters of mercury at 1000° , a copper deficiency of about 10^{-3} gram atoms of Cu. The deviations from the stoichiometric composition are thus smaller by several powers of ten than in the case of ferrous oxide. In contrast to this result are the analytic determinations of the copper content in cuprous oxide by Frohlich (reference 20). According to reference 20, there is a copper excess of about 0.2 percent Cu (mean value of the analyses given). There is as yet no explanation of the difference in the results.

The investigation procedure of Wagner is considered more reliable than the analytical observation. A copper deficiency in the cuprous oxide, is therefore assumed herein.

With regard to the oxides of the remaining metals, it is known that in the case of zinc oxide (reference 21), cadmium oxide (reference 21), aluminum oxide (reference 22), and tantalum oxide (reference 22), the conductivity decreases with the oxygen pressure; that is, there exists an excess of metal. On account of the small size of the metal ions (Zn^{++} , 0.85 Å; Cd^{++} , 1.05 Å; Al^{+++} , 0.55 Å; and Ta^{++++} , 0.7 Å; values from reference 23), von Baumbach and Wagner (reference 21) assumed the excess metal ions to occupy intermediate places in the lattice.

In the case of most of the metal oxides, however, there are as yet no investigation results. From the magnitude of the ion radii, it is to be expected that only the metal ions travel in the oxides since the ion radius of the oxygen, which increases to 1.3 Å by taking up two electrons, exceeds the ion radii of the technically applied metals, size of which has been decreased by the giving up of electrons (reference 23). The new lattice planes of the oxide layer therefore arise at the oxide-air boundary. If the oxide layer is formed without defects, the oxidized body is of the form of figure 2.

If the oxygen ions were to travel, new lattice planes would arise at the oxide-metal boundary and would form an oxidized body of the form of figures 3 and 4. It is not to be concluded, however, that the occurrence of this form of oxidized body indicates a traveling of the oxygen ions. By periodic scale formation, the formation of new lattice planes, even when occurring at the boundary between the oxide and air, may always be displaced again in the neighborhood of the boundary between the oxide and the metal. The travelling of the metal ions may thus lead to both forms of the oxidized body. From the foregoing discussion it is to be concluded that travel of the metal ions also occurs in the case of the oxides of tungsten, magnesium, and calcium.

In the foregoing considerations, the fact that some metals form oxide layers of several oxides was not taken into account. Of the technically important metals, the following belong to this group: iron (FeO , Fe_3O_4 , and Fe_2O_3) and copper (Cu_2O and CuO). According to the investigations of H. H. v. Baumbach, H. Dunwald, and C. Wagner (reference 24), the electrical conductivity depends very little on the oxygen pressure. The transport number of the Cu^{++} ions was very low ($n_{\text{Cu}^{++}} < 5 \cdot 10^{-3}$) and lay within the experimental errors. The copper oxide should therefore strongly check the oxidizing of the copper. According to the measurements of Feitknecht (reference 3), the oxidizing rate increases at low oxygen pressures below the equilibrium pressure, over $\text{Cu}_2\text{O} + \text{CuO}$, with increasing oxygen pressure of the gas and becomes constant when equilibrium is attained. With the formation of CuO , therefore, the oxidizing rate of the copper decreases but not indefinitely. Further oxidation is merely retarded. The CuO layer probably forms no dense coating. This is also indicated by the fact that a transition from

Cu_2O to CuO is followed by a decrease in volume. The details of the phenomena are not yet clear.

In the case of both copper and iron the metal ions in the oxide poorest in oxygen are the most mobile. Correspondingly, the width of this layer is greatest.

Oxidizing Alloys

The sequence of oxide formation. - In the case of alloys, the oxides of the different alloy components are formed and in some cases the oxides are combined with each other (for example, Fe_2SiO_4). In figure 5 is shown the simplest case for an alloy of two components. In this case only, the two metals and their oxides occur. The changes in a thin boundary layer of a mixture are now considered. As a result of the oxidation, the composition of the layer is displaced along the ray XO from X to O. The composition of the layer first reaches the field $A + B + \text{BO}$. Only the crystal type B is therefore oxidized until the ray XO intersects the straight line $A + \text{BO}$, at which point the total B of the layer under consideration is oxidized. As the oxidation proceeds, the boundary layer reaches the field $A + \text{AO} + \text{BO}$ so that the oxidation of A is begun. The oxidation is ended when the ray XO has reached the straight line $\text{AO} + \text{BO}$.

Figure 6 represents a somewhat more complicated case. In addition to the oxides AO and BO , the compound AO BO occurs. During the oxidation there is at first formed BO , then AO BO with the oxidation of A and the reaction of the AO with the already existing BO , and finally there is also formed AO . The more complicated cases may be similarly described.

In the two cases considered, A may be said to be more noble than B. If considerations are restricted to the lowest oxidation stage of each metal and to the alloys of two metals, the metals can thus be arranged in an oxidation series such that each metal is oxidized earlier than the following metal in the series (reference 25). For the corresponding case of the sulphides, G. Tammann and H. v. Samson-Himmelstjerna (reference 26) have experimentally determined the sequence of the metals. "In the case of the oxidation series, corresponding direct tests are unavailable. It is possible, however, by listing the elements according to the decreasing heats of formation of their lowest oxides, referred to the heat of formation of an oxide MeO , to assign the place of a metal in the oxidation series."

Objections have been raised as to whether it is justifiable to put the heats of formation, referred to MeO , at the basis of the considerations. This question will therefore be discussed with the aid of

figure 7. It is assumed that the heats of formation are the only determining factors for the free energy. The oxide B_2O is less noble than AO because the straight line $A+B_2O$ lies above the dotted line $B-AO$. In order for this to hold for other oxides B_xO_y , for example, for BO , the straight line BO must lie above BO . As a measure of the affinity, it is possible to use either the angle between BO and BO as was done by Guertler (reference 25), or the value which is assumed by the straight line BO at a special point, for example, for the composition BO . The second measure was used in table 1. In column 1 of this table is given the chemical symbol; in column 2, the formula of the oxide poorest in oxygen content; in column 3, its heat of formation; and in column 4, the heat of formation referred to the oxide MeO .

The sequence of the table corresponds to the oxidation sequence at room temperature under the assumption that the free energy is determined primarily by the heat of formation. For values lying near each other, deviations may occur because, on the one hand, other factors help to determine the free energy, and, on the other hand, because the heat of formation at the oxidation temperature was necessarily used as a basis for the considerations. For this reason, copper, for example, is not placed in the sequence of heats of formation but according to the observations on oxidation.

Changes in the sequence in the case of alloys of two or more metals can also be brought about by the formation of compounds among the individual oxides. Thus, for example, the sequence for the silicates does not always agree with that for the oxides. For a complete description, therefore, the sequence of the oxides must be supplemented by further sequences of the compounds. This, however, is not as yet possible.

Distribution of oxides in oxidation layer. - For the formation of the oxide layer structure, it is of importance that the oxides of the added substances should be concentrated at definite points, namely at the boundary between the oxide and the metal. In the derivation of this rule, it was assumed that the oxide AO for B , and similarly BO for A , have no solubility. It is further assumed that the more noble metal A is present in strong excess. The less noble oxide BO is then formed first on the surface. The practical importance of the production of alloys resistant to oxidation, will be discussed later. For the following discussion it will be assumed that gaps in which AO may be formed exist in the BO layer. In both types of crystal, further growth of the layer occurs by diffusion through the oxide crystals, where, on account of the absence of solubility of the two oxides, the A ions travel only through the AO layer and the B ions only through the BO layer, forming new lattice planes at the oxide-air boundary. The velocity of this process is determined to a large extent by the concentration of B or A so that

more AO than BO forms per unit of time. The AO finally predominates over the BO because it continues to increase at the boundary between the oxide and the metal. Furthermore, the A atoms travel partly around the BO particles so that BO is partly displaced toward the middle of the metal specimen.

The result is an accumulation of BO at the oxide boundary. In the case of iron alloys this could be shown by analysis of the separable oxide layers (reference 6). In figure 8 the measurements on iron-aluminum alloys are shown as an example. The distance from the equal distribution line is a measure of the concentration. At temperatures above 1000° the increased concentration of the aluminum in the boundary layer between the oxide and the alloy is particularly large. The concentration of the less noble alloying metal at the boundary between the oxide and the metal occurred in the case of all iron alloys with the exception of the manganese steels (reference 6). In the case of the copper alloys, the rule was similarly followed in many instances, according to reference 20.

If the metal A in excess is less noble than B, AO is produced first and the B is concentrated at the oxide-metal boundary. At that place, however, it cannot be oxidized, since the more readily oxidizable A is present. Because thickening of the layer is produced at the oxide-air boundary, nothing is changed until the concentration of B at the oxide boundary forms a layer excluding A, and further oxidation can proceed as though the more noble B were in excess. There is also produced BO until the excess has again been reduced to a certain amount. The over-all result of these changes is a concentration of the more noble metal at the oxide-metal boundary. It was shown to be present in the oxide of several iron alloys (reference 6), and in copper-silver alloys rich in copper (reference 20).

It has therefore been shown that the elements which as a rule are found in smaller quantities concentrate at the oxide-metal boundary. However, if the metal exists in excess the concentration is in oxide form if the added substance is less noble and in metallic form if it is more noble.

The picture of the oxidation process developed in this paper is greatly schematized but nevertheless represents main features. Further insight is provided by the structure of the oxide boundary. As an example, figure 9 shows the structure of a steel with 4 percent Al, which was oxidized for 5 hours at 1000°. The aluminum oxide, which can be well distinguished from the iron oxides by its color, reached into the iron layer. These penetrating oxides can be produced only because the oxygen, in spite of its low solubility in iron, penetrates the iron and there oxidizes the aluminum. It is probably not a question of a

real solubility, but a penetration along boundary surfaces or grain boundaries. As soon as oxygen attacks an aluminum atom, it reacts with the atom and, as aluminum oxide, attaches itself to already existing aluminum-oxide crystals or forms new nuclei. This process would result in a gradual growth of aluminum oxide filaments in the interior of the steel, if the metal boundary did not at the same time increase toward the interior through the formation of the iron oxide. Because the iron enters the oxide layer, the iron between the aluminum oxide filaments disappears and the aluminum oxide concentrates in the neighborhood of the oxide boundary.

The more steadily the state of penetration of the aluminum oxide filaments from the oxide layer is retarded, the less the oxidizing force of the gas becomes. In the case of weakly oxidizing gases, the oxide layer may therefore penetrate deep into the material and strongly damage it. This occurs in the case of cast iron, those graphite veins of which form paths for the penetration of the oxygen into the interior layers of the cast iron. The oxidation proceeds from the graphite veins. The oxygen concentration is, however, still small enough so that at first no iron oxides are formed but only iron silicates from the silicon content of the cast iron (reference 27). It is only after this process has continued for some time and the graphite veins have largely vaporized that iron oxides are formed at the location of the previous graphite veins. Figure 10 shows an oxidized cast iron. In place of the graphite veins, magnetic iron oxide has already largely been formed. From the graphite veins a very finely distributed mass of iron and iron silicate is formed.

Oxidation-resistant alloys. - The question arises whether more noble or less noble substances are to be added. Both are concentrated at the boundary between the metal and oxide and it may be presumed that a thick layer could be formed which would effectively check the further progress of the oxidation reaction. It is here necessary to observe, however, that the noble metals permit the passage of oxygen. Frohlich (reference 20) has shown that the galvanic silvering of copper does not protect it against oxidation. The thickness of the layer is a factor, but it is hardly to be expected that a thicker layer is formed in the oxidation than in the galvanic silvering. In many cases, in particular in the oxidation of nickel steels (reference 28), a strong nickel layer containing oxide is formed. Aside from the expense, however, there is hardly to be expected any considerable protection against oxidizing through alloying a more noble metal with the basic metal.

All oxidation-resisting alloys contain a less noble element as the essential material for reducing the oxidation. The oxidation-resistant chrome-nickel steels (in which there is added to the iron a more noble element, nickel, and a less noble element, chromium) are no exception, because the element that essentially increases the resistance to oxidation is chromium (reference 6).

In order that there may be considerable protection against oxidation, a thick layer of the oxide of a less noble alloying metal must be formed on the alloy. The rate of travel of the metal ions in this layer must be very low because the thickening of the layer depends on it.

How great the difference in the oxidizing action may be is shown by figure 11 taken from a paper by Portevin, Pretet, and Jolivet (reference 29). As long as the aluminum steel with 8.5 percent Al was covered only by the white aluminum oxide, the weight added through oxidation was very small. Starting from a definite moment, which for the individual specimens occurred at various times, a considerably stronger oxidizing action associated with the formation of the iron oxides began because the aluminum oxide layer had contained gaps at some places. A further condition is that the secondary oxide form a dense protective coating.

It is further necessary that the melting point of the secondary oxide layer and also the melting point of its mixture with the oxide of the basic metal, as well as with further added substances of the alloy, lie appreciably above the oxidation temperature. Thus the limit, for example, of the oxidizing resistance of silicon steels, is determined by the melting point of the eutectic of ferrous oxide and fayalite (Fe_2SiO_9) at 1240° . At 1200° the silicon steels are no longer resistant to oxidation. Similarly, the contact with substances which are capable of reacting with the secondary oxide effect a transition from protection against oxidation to a strong oxidizing attack. In this sense, most of the metal oxides react with the oxide layers of the oxidation-resistant alloys.

The conditions for the formation of protecting oxide layers are best satisfied in the case of substances which in the ceramic industry are employed as fire-resistant substances, for example, aluminum oxide, silicic acid, chromium oxide, magnesia, and beryllium oxide.

SUMMARY

The oxidation of metals occurs by diffusion of the metal ions through the oxide layer. The new lattice planes are thus formed at the surface of the oxide layer. If scale is formed, the place of the oxide formation is displaced toward the neighboring interior surface of the metal surface. Through periodic formation of scale, the oxidation may proceed linearly with the time.

In the case of alloys, the oxides of the various alloy elements are to a first approximation formed in the order of the heats of formation. The added alloys tend to concentrate at the boundary between the

oxide layer and the metal when they are less noble or more noble than the base metal existing in excess. The conditions are set up for the formation of oxide-resistant layers on alloys.

Translated by S. Reiss
National Advisory Committee
for Aeronautics

REFERENCES

1. Tammann, G.: Z. anorg. allg. Chem. Bd. 111, 1920, p. 78.
2. Pilling, N. B., and Bedworth, R. E.: J. Inst. Met., Bd. 29, 1923, p. 529.
3. Feitknecht, W.: Z. Elektrochem, Bd. 35, 1929, p. 142.
4. Tammann, G., and Koster, W.: Z. anorg, allg. Chem., Bd. 123, 1923, p. 196.
5. Masing, G.: Die Korrosion der metallischen Werkstoffe, I, 1936, p. 97/119.
6. Scheil, E., and Kiwit, K.: Arch. Eisenhuttenw., Bd. 9, 1935/36, p. 405.
7. Fischbeck, K.: Z. Elektrochem., Bd. 39, 1933, p. 316.
8. Pfeil, L. B.: J. Iron Steel Inst., vol. 119, 1929, p. 501.
9. The author is indebted to Head Engineer C. Drescher, Siemens-Schuckert-Werke for the specimens.
10. Private communication by Dr. P. Wiest.
11. Wagner, C.: Z. angew. Chem., Bd. 49, 1936, p. 735.
12. Steiheil, A.: Ann. Phys., Bd. 19, 1934, p. 465.
13. Finch, G. J., and Quarrel, A. G.: Nature, vol. 131, 1933, p. 877.
14. Wagner, C.: Z. phys. Chem., Bd. 21, 1933, p. 25.
15. Schenk, R., and Tingmann, T.: Z. anorg. alg. Chem. Bd. 166, 1927, p. 113; see also M. Hansen, Zweistoffsysteme, J. Springer Berlin, 1936.

16. Jette, E. R., and Foote, F.: J. Chem. Physics, vol. 1, 1933, p. 29.
17. Hagg, G., and Sucksdorff, J.: Z. phys. Chem., Bd. 22, 1933, p. 444.
18. Hagg, G., and Klingstrom, A. L.: Z. phys. Chem., Bd. 22, 1933, p. 453.
19. Dunwald, H., and Wagner, C.: Z. phys. Chem., Bd. 22, 1933, p. 212.
20. Frohlich, K. W.: Z. Metallkde., Bd. 28, 1936, p. 368.
21. von Baumbach, H. H., and Wagner, C.: Z. phys. Chem., Bd. 22, 1933, p. 199.
22. Hartmann, W.: Z. Phys., Bd. 102, 1936, p. 709.
23. Remy, H.: Lehrbuch der anorganischen Chemie, Akademische Verlagsgesellschaft (Leipzig), 1931, p. 19.
24. von Baumbach, H. H., Dunwald, H., and Wagner, C.: Z. phys. Chem., Bd. 22, 1933, p. 226.
25. Guertler, W., and Leitgeb, W.: Vom Erz zum metallischen Werkstoff. Akad. Verlagsges. (Leipzig), 1929, p. 297.
26. Tammann, G., and von Samson-Himmelstjerna, H.: Z. anorg. allg. Chem., Bd. 216, 1934, p. 288.
27. Scheill, E.: Arch. Eisenhüttenw., Bd. 6, 1932/33, p. 61.
28. Houdremont, E.: Sonderstahlkunde, J. Springer (Berlin), 1935, p. 180.
29. Portevin, A., Pretet, E., and Jolivet, H.: Rev. Metallurg., vol. 31, 1934, p. 219.

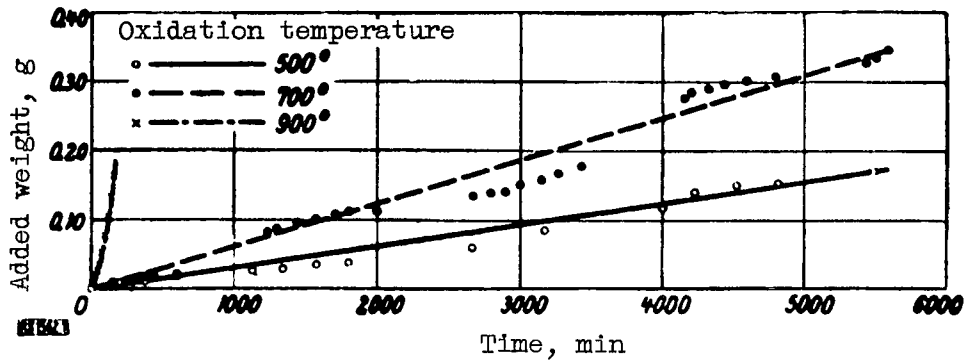
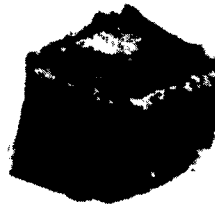


Figure 1. - Oxidation isotherms of tungsten



RS1562.2

Figure 2. - Oxidized specimen of copper.



RS1562.3

Figure 3. - Oxidized specimen of tungsten.

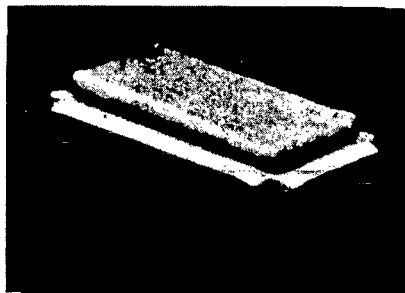


Figure 4. - Oxidized specimen of widia.

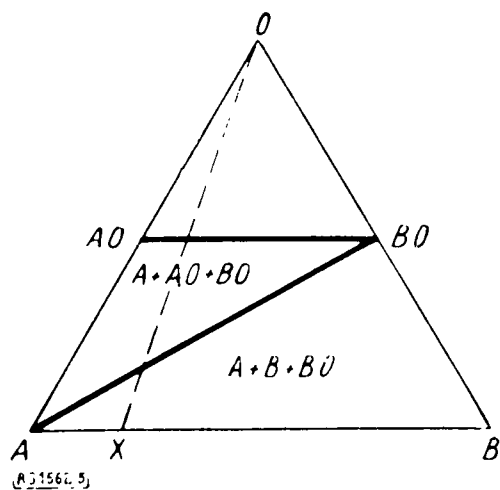


Figure 5. - Sequence of the formation of oxides; B less noble than A.

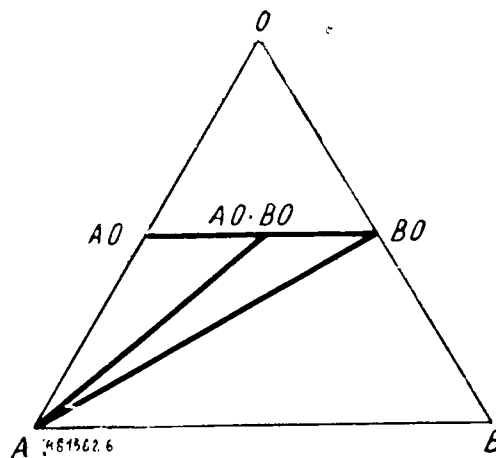


Figure 6. - Sequence of the formation of oxides, combining of oxides; B less noble than A.

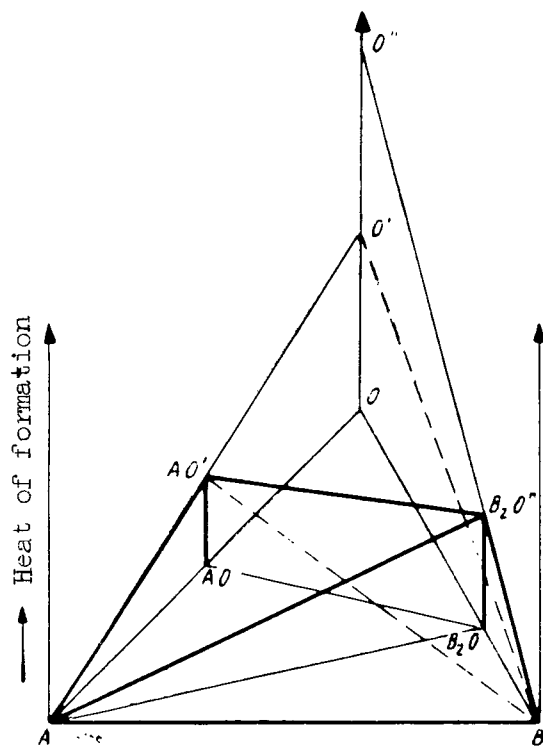


Figure 7. - Relation between heats of formation and equilibria.



Figure 9. - Structure of the oxide boundary of a steel with 4 percent Al after 5 hours heating at 1000° .



Figure 10. - Structure of oxide (iron silicate) in cast iron.

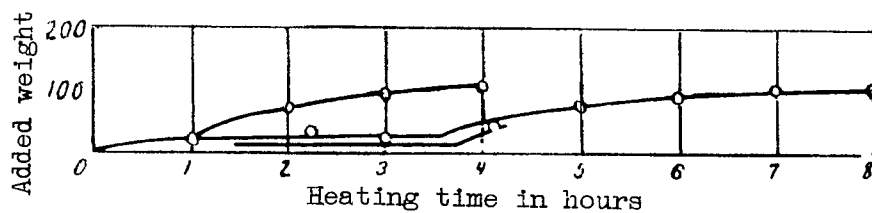


Figure 11. - Oxide isotherms of aluminum steel with 8.5 percent Al at 1000° (according to A. Portevin, E. Prétel and H. Jolivet).

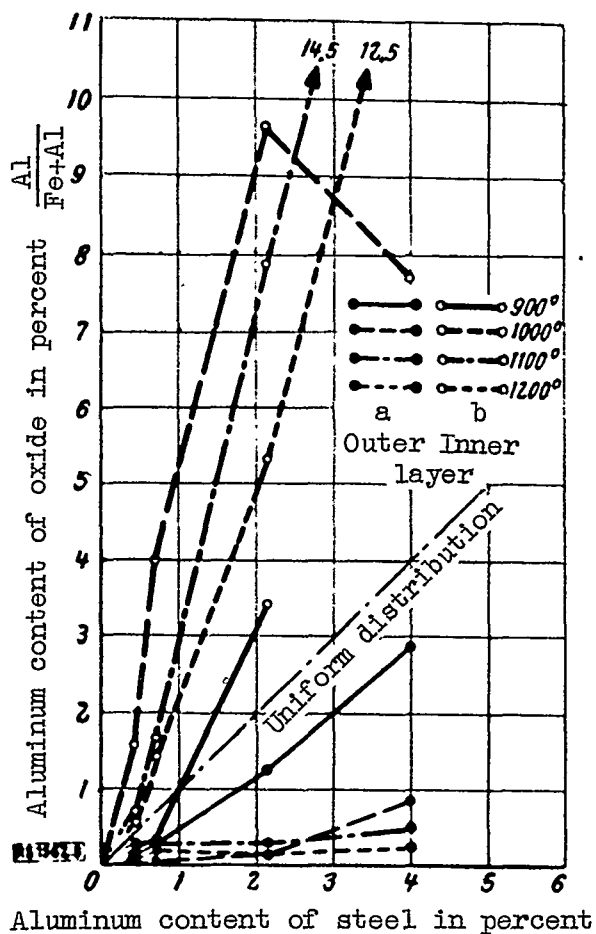


Figure 8. - Aluminum content in various oxide layers of aluminum steels.

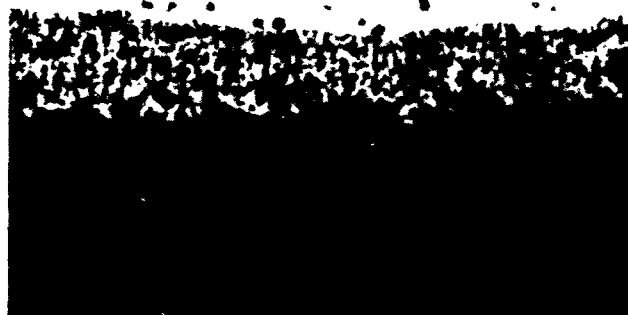


Figure 9. - Structure of the oxide boundary of a steel with 4 percent Al after 5 hours heating at 1000° .



Figure 10. - Structure of oxide (iron silicate) in cast iron.

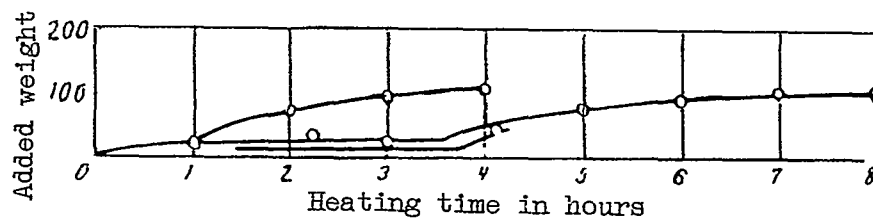


Figure 11. - Oxide isotherms of aluminum steel with 8.5 percent Al at 1000° (according to A. Portevin, E. Prétel and H. Jolivet).

NASA Technical Library



3 1176 01440 4629